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Hydrometallurgical Container Material on the Loss of Silver, Mercury and Copper Ions from Aqueous Solutions



TECHNICAL BULLETIN NO. 69
(Résumé en français)

INLAND WATERS DIRECTORATE
WATER QUALITY BRANCH
OTTAWA, CANADA, 1972.

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Influence of Container Material on the Loss of Silver, Mercuric and Cupric Ions from Water Solutions

Ivan Sekerka and Josef F. Lechner

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Abstract

The influence of container material on Ag^+ , Hg^{++} , and Cu^{++} ion losses from acidified and untreated water samples at room and refrigeration temperatures during short- and long-term storage is described. Standard sample solutions were tested in Teflon, polypropylene, polyethylene, flint-glass and Pyrex-glass bottles. The losses of metal ions were determined at intervals varying from 2 to 1000 hrs. Ion-selective electrodes were used for all measurements. Teflon was by far the superior container material. Acidification of samples reduced considerably the losses of all ions.

Résumé

Ce rapport décrit l'influence de la nature du matériel d'un récipient sur les pertes d'ions Ag^+ , Hg^{++} et Cu^{++} contenus dans des échantillons d'eau non traités, acidifiés, se trouvant à des températures ambiantes ou refroidies et analysés après des périodes variables d'emménagement. Pour ce faire, des solutions standard ont été testées dans des bouteilles en Téflon, polypropylène, polyéthylène, en verre de plomb et en pyrex. Les pertes d'ions métalliques ont été déterminées à intervalles variant de 2 à 1000 heures, en utilisant des électrodes sélectives d'ions. Le Téflon s'est avéré être de loin le meilleur matériel testé. De même, l'acidification des échantillons a considérablement réduit les pertes pour tous les ions.

Influence of Container Material on the Loss of Silver, Mercuric, and Cupric Ions from Water Solutions

Ivan Šekerka and Josef F. Lechner

INTRODUCTION

The increasing awareness of the important role of trace elements in water has greatly stimulated the refinement and extension of analyses at these levels. The analytical requirements imposed by the minute quantities and typically complex systems involved, have led to the development of methodology and instrumentation so specialized that it warranted consideration of a distinct field in analytical chemistry (Morrison, 1965; Afghan, in press; Mizuike, 1965).

Basically, chemical analysis of water samples consists of the following major steps:

- I) sampling and preservation
- II) transportation and storage
- III) preparation and preconcentration
- IV) chemical analysis

To obtain correct results, emphasis must be given to all steps.

There are many indications that no extreme difficulties are encountered in withdrawing representative water samples. However, serious problems may occur during the transport and storage. The original chemical composition may, and usually will, change during this time. These changes are especially important in respect to trace components of the water samples. Because of their extremely low concentration and very small absolute amount, trace elements are likely to be lost. Generally speaking, the lower is the concentration of trace elements, the higher is the danger of loss (Matson *et al.*, 1966).

After a water sample is taken it should be treated to preserve its original composition unaltered until it is analysed. The physical, chemical, and biological processes causing changes in the chemical composition of water samples during transportation and storage have been thoroughly studied (Eichholtz *et al.*, 1965; West *et al.*, 1966). Durst and Duhart (1970) estimated silver-ion adsorption on container surface by a potentiometric method using a silver-ion selective electrode. The study indicates that none of the tested materials (Pyrex glass, polyethylene, Vycor, and Teflon) is really suitable for long-term storage of solutions which contain low levels of silver ion.

Our investigation was designed to give estimates of the amounts of metal ions lost in containers of various materials and to determine the most suitable storage container and storage condition of water samples containing low levels of heavy-metal ions.

Possible methods for water samples pretreatment, e.g., extraction, ion-exchange, and electrolysis were not investigated in detail. However, preliminary experiments indicated that they are unacceptable because of requirements of relatively complicated operations demanding skill and inherently carrying the danger of secondary contamination and further losses.

EXPERIMENTAL

Electromotive force (EMF) measurements were taken with Orion 94-16 (silver), 94-53 (mercury) and 94-29 (cupric) ion-selective electrodes, in conjunction with a double-junction reference electrode. The EMF values were taken to the nearest 1mV, using an Orion 801-digital-pH meter, Orion-855 automatic switch, and Orion-851 digital printer.

Stock solutions, $1 \times 10^{-2}M$, of $Hg(NO_3)_2$, $AgNO_3$, and $Cu(NO_3)_2$ were prepared from reagent grade chemicals according to the basic analytical chemistry literature (Vogel, 1961). From the stock solutions, several electrode-calibration solutions, between 1×10^{-4} and $1 \times 10^{-8}M$, were prepared by serial dilution. An equal amount of ionic-strength adjustor ($0.1M KNO_3$) was used for all measurements. During the calibration of the ion-selective electrodes as well as during the measurements of samples the solutions were stirred magnetically at a constant rate and EMF readings were taken after an arbitrary stabilization period of 5 minutes for each sample. The measurements were carried out at constant temperature of $25 \pm 1^\circ C$. The data obtained from standard solutions were used for the construction of calibration curves, which served to relate observed EMF readings to the metal-ion activity (Fig. 1).

In order to eliminate EMF drift during the actual measurements, spot-check measurements of a freshly prepared standard solution were performed. If drift was detected an EMF drift correction was applied to each test-solution reading. Taking into consideration the detection limits of ion-selective electrodes — $1 \times 10^{-8}M Hg^{2+}$ (Orion newsletter, 1970), $1 \times 10^{-7}M Ag^+$ and $1 \times$

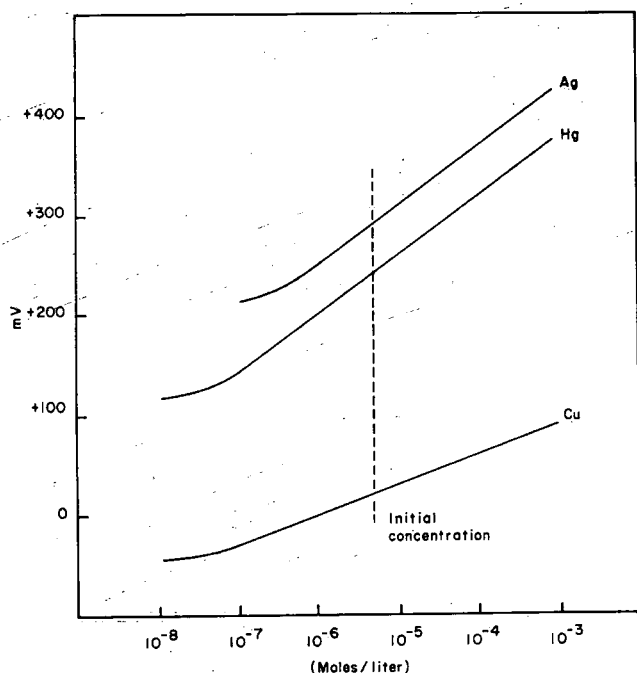


Figure 1. Calibration curves of ion-selective electrodes.

10^{-8}M Cu^{2+} (Durst, 1969) — and our previous results (Sekerka *et al.*, in press) as well as the expected levels of metal-ion losses, it was decided that the most suitable initial metal-ion concentration was $5 \times 10^{-6}\text{M}$. At this concentration, mercury, silver, and cupric ion-selective electrodes exhibit the Nernstian response to the activity of the ion of interest and the amount of ion in the sample is sufficiently low to obtain measurable changes of the ion's activity.

The container materials tested in this study were: flint glass, Pyrex glass, polyethylene, polypropylene and Teflon. New, 1000-ml bottles were washed with detergent solution, then with concentrated HNO_3 , and rinsed repeatedly with double-distilled water, then air dried. Standard metal ion solution ($5 \times 10^{-6}\text{M}$), 1000 ml, was then added to each of the test bottles. Since it was our objective to test metal losses under more than one condition, the following procedure was used. Eighteen bottles of each material were tested. Containers Nos. 1 to 6 were filled with silver solution, Nos. 7 to 12 with mercury solution, and Nos. 13 to 18 with copper solution. The solutions in bottles Nos. 1 and 2, 7 and 8, and 13 and 14 were acidified with diluted HNO_3 to pH 1 and kept at room temperature. Solutions in containers Nos. 3 and 4, 9 and 10, and 15 and 16 were not acidified and also kept at room temperature. The remaining bottles Nos. 5 and 6, 11 and 12, and 17 and 18 were kept in the refrigerator at $+5^\circ\text{C}$. This procedure was uniform for all five tested container materials. For the measurements, 25 ml of the test solution were withdrawn from the test bottle and placed into the 100-ml Teflon beaker. Previously acidified samples were neutralized to pH 6 with 1.0 M KOH

solution; refrigerated samples were brought to room temperature. After a standard addition of 2 ml of ionic-strength adjustor (0.1 M KNO_3) the measurement of EMF took place. The EMF of each sample was measured at intervals of 2, 4, 8, 16, 32, 64, 125, 250, 500 and 1000 hrs. The values of EMF were converted to the concentration via calibration curve and the percent losses were calculated from the equation:

$$\% \text{ loss} = \frac{\text{Me}_0 - \text{Me}_t}{\text{Me}_0} \times 100$$

where

Me_0 = original concentration of metal ion ($5 \times 10^{-6}\text{M}$)
 Me_t = average metal-ion concentration taken from the measurement of two bottles of the same group and container material at time t , after the introduction of the solution into the bottles.

The 1000-hr cycle was repeated three times after washing the bottles according to the procedure mentioned above.

RESULTS

Observed loss (%) for mercury, silver, and copper of tested container materials during the period from 2 to 1000 hrs are summarized in Tables 1, 2 and 3. All reported losses (%) are mean values with maximum variations of up to 3%. For all practical purposes, the three metal ions were absorbed at a similar rate. However, there was a tendency of the silver ion to show, initially, slightly higher losses than the mercuric and cupric ions. No preferential absorption could be observed at the end of the 1000-hr test period. No difference was observed by repeated use of the containers.

Untreated Samples

In Table 1, all samples display relatively high losses. Teflon inflicted losses of 5% after 64 hrs and 32% after 1000 hrs. The losses in polypropylene bottles reached 12% and 40%, in flint glass 21% and 36%, in polyethylene 30% and 47% and in Pyrex glass 38% and 54% after 64 and 1000 hrs, respectively. Teflon caused the lowest loss and Pyrex glass the highest loss. The largest losses occurred within the first 100 hrs of storage.

Samples Acidified to pH 1

In Table 2, it is evident that acidification of samples decreased losses of metal ions very significantly. Again Teflon has the best record, reaching 1% after 64 hrs and 6% at the end of the test period. This compares to Pyrex glass with 8% at 64 hrs and nearly 20% after 1000 hrs of storage time. All other test containers were in between flint glass reaching 3% and 11%, polypropylene 3 and 12% and polyethylene 7 and 17% after 64 and 1000 hrs, respectively.

Table 1. Percentage losses for $5 \times 10^{-6}M$ solutions of silver, mercury, and copper on surfaces of various containers at pH 6 and at room temperature.

Container -material	2 hr			4 hr			8 hr			16 hr			32 hr			64 hr			125 hr			250 hr			500 hr			1000 hr		
	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu
Teflon	2	2	2	2	2	2	3	3	3	3	3	3	4	4	4	5	5	4	12	10	10	17	14	18	25	21	20	33	30	32
Polypropylene	2	2	2	3	3	2	5	4	5	7	6	6	9	9	7	12	11	12	22	20	21	28	25	23	36	32	31	40	39	37
Polyethylene	6	5	6	12	10	11	18	18	15	23	20	21	27	24	25	31	29	29	35	32	33	38	36	32	42	39	40	48	45	46
Flint glass	4	5	5	9	7	9	12	10	10	15	15	13	19	17	18	21	20	20	25	22	23	27	29	25	34	30	31	37	34	35
Pyrex glass	10	10	8	16	14	14	22	20	21	28	28	27	33	30	31	39	37	37	47	44	46	50	50	48	53	50	51	55	53	54

Table 2. Percentage losses for $5 \times 10^{-6}M$ solutions of silver, mercury, and copper on surfaces of various containers at pH 1 and at room temperature.

Container -material	2 hr			4 hr			8 hr			16			32 hr			64 hr			125 hr			250 hr			500 hr			1000 hr		
	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu
Teflon	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	2	2	2	2	2	2	4	4	4	6	6	6
Polypropylene	0	0	0	0	0	0	0	0	0	1	1	2	2	2	3	3	3	3	5	4	4	7	6	5	9	9	8	12	11	12
Polyethylene	0	0	0	2	1	2	3	3	3	3	4	5	4	5	5	7	7	6	8	8	8	10	11	10	14	15	15	17	16	16
Flint glass	0	0	0	0	0	0	0	0	0	1	0	1	2	2	2	3	2	2	4	3	3	6	6	6	7	8	7	10	11	10
Pyrex glass	0	0	0	2	2	1	4	3	4	5	4	5	7	6	6	8	7	8	10	10	9	12	11	10	15	16	16	19	18	19

Table 3. Percentage losses for $5 \times 10^{-6}M$ solutions of silver, mercury, and copper on surfaces of various containers at $5^{\circ}C$ and pH 6.

Container -material	2 hr			4 hr			8 hr			16 hr			32 hr			64 hr			125 hr			250 hr			500 hr			1000 hr		
	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu	Ag	Hg	Cu
Teflon	0	0	0	0	0	0	2	2	2	3	3	3	4	3	3	4	4	4	6	5	6	10	9	9	16	14	15	25	21	22
Polypropylene	2	0	0	2	2	2	3	2	3	4	4	4	6	5	4	7	7	6	10	8	9	13	13	14	21	19	20	31	30	29
Polyethylene	2	2	2	5	4	3	7	7	6	12	10	11	15	15	16	20	17	18	25	24	24	32	30	29	35	35	33	38	35	35
Flint glass	0	1	0	3	2	3	4	4	3	6	5	6	9	7	8	10	9	9	12	13	11	14	15	15	19	21	20	30	30	31
Pyrex glass	3	2	1	6	6	7	9	10	8	14	12	12	18	19	17	23	20	21	28	30	29	35	33	32	40	41	39	44	43	44

Samples stored at 5°C

In Table 3 it is shown that the lower temperature slows down the rate of loss of metal ions in water samples by approximately 10% for all tested materials in comparison to the samples stored at room temperature. Teflon is best with 4% after 64 hrs and 23% after 1000 hrs; polypropylene is second with 7% and 30% followed by flint glass with 9% and 30%, polyethylene with 19% and 36%, and, finally, Pyrex glass with 21% and 44% after 64 and 1000 hrs, respectively.

CONCLUSIONS

Based on our results, Teflon is by far the superior container material of all the materials tested, as far as metal ion losses is concerned, over short and long storage periods. The higher price of Teflon may be a problem. The price per 1000-ml Teflon bottle is still over 10 dollars at the present time, i.e., more than 10 times the price of polypropylene or polyethylene bottles. Nevertheless, Teflon bottles should be a worthwhile investment, considering the advantageous properties of Teflon for water sample preservation during transport and storage as well as its durability and the possibility of repeated use for long periods.

Acidification of samples to pH 1 reduced losses of ion considerably; consequently it should be applied whenever it is possible. For short-term storage — periods up to 48 hrs — Teflon exhibited losses of less than 5% which is adequate for such periods without acidification. For storage intervals of more than 48 hrs, none of the materials tested was satisfactory; acidification would appear to be essential. Storing the samples at lower temperature reduced losses. However it is not significant enough to warrant application.

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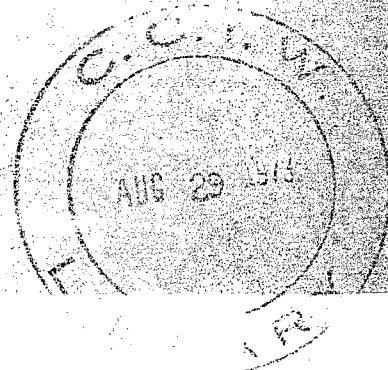
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